

CONTROL OF H₂S EMISSIONS USING AN OZONE OXIDATION PROCESS.
PRELIMINARY RESULTS.

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16. Abstract The problem of eliminating industrial emission odors does not have a simple solution, and consequently has not been researched extensively. Therefore an experimental research program regarding oxidation of H ₂ S through ozone has been undertaken to verify the applicable limits of the procedure and, in addition, was designed to supply a useful analytical means of rationalizing the design of reactors employed in the sector. <div style="text-align: center;">ORIGINAL PAGE IS OF POOR QUALITY</div>					
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CONTROL OF H₂S EMISSIONS THROUGH OZONE OXIDATION PROCESS.
PRELIMINARY RESULTS.

D. De Faveri, B. Ferrando, and G. Ferraiolo

This article covers the first results obtained, which /463* indicate that, for high efficiency, it is necessary to use high concentrations of ozone at the reactor inlet, since holding times greater than 4-6 sec are of negligible value.

Control and containment of irritating effects of odorous emissions are usually difficult, since the olfactory threshold of the compounds responsible for the phenomenon is normally extremely low. Technological resources in this case generally rely on control systems using one or more of the following processes [1, 2]:

- chemical (for example, oxidation, thermodestruction-incineration);
- physical (for example, absorption- and adsorption-activated carbons and similar);
- biological (for example, enzymatic oxidation).

Of particular interest among the chemical processes is ozone oxidation developed for wet way (aqueous phase) or for direct gas-gas interaction [3, 4]. Corresponding to this solution is an initial scheme involving the relatively simple development of a process-system with intrinsic technical-economical advantages for the construction and operation /464 of plants which, in addition, have lower energy requirements. Nevertheless, these are rarely considered in the usual "ecological" applications. This may be justified, in part, because the process requires the use of O₃, a non-marginal reagent; but it appears more likely to single out the principal

*Numbers in the margin indicate pagination in the foreign text.

obstacles encountered in designing oxidation reactors. These uncertainties are tied to the reaction kinetics among the odorous compounds and the ozone, as well as to the speed with which these odors naturally disappear.

Under particular circumstances, in fact, the ozone exhibits a very brief "lifetime," where it rapidly reaches concentrations so low as to render any oxidation process extremely difficult [3]. This leads to a rapid loss of O_3 over time, with consequent lessening of the true speed of oxidation. It therefore appeared useful to thoroughly examine the kinetic mechanisms mentioned above with the dual goal of:

- verifying the limits of the actual practice of the ozone oxidation process,
- developing an analytical instrument to improve and rationalize the design of the oxidation reactor.

For this purpose, we utilized a laboratory reactor in which a medium-low concentration of the odorous substance H_2S (frequently found in odorous emissions) was used.

Oxidation Kinetics

In the reaction between H_2S and ozone, the speed with which ozone disappears is not due solely to the oxidation of H_2S , but also to its decomposition, intensified by the presence of the latter, from the same ozone (5), as recorded at the beginning.

The respective reaction and decomposition speeds, as a function of the disappearance of H_2S and O_3 may be expressed by means of general equations as follows:

$$-\frac{d[H_2S]}{dt} = k_1 [H_2S]^m [O_3]^n \quad (1)$$

$$-\frac{d[O_3]}{dt} = k_2 [O_3]^p [H_2S]^q \quad (2)$$

Therefore, the decomposition of the ozone is considered to be a reaction parallel to the first, even though catalyzed by the presence of H_2S [5].

This decomposition, through which it is possible to hypothesize kinetics of the second order [5], in fact determines the decline in time of the ozone concentration.

Since, therefore, $p = 2$ and $q = 0$ [5], integration of equation 2 produces the following expression:

$$[O_3] = \frac{[O_3]_0}{[O_3]_0 t k_2 + 1} \quad (3)$$

in which

$$[O_3] = [O_3]_0 \quad \text{per } t=0$$

In the presence of H_2S as well, the initial concentration of O_3 diminishes within a time period of about 2 sec [5].

Assuming this condition, by combining equation 3 with equation 1 and integrating the latter, we obtain:

$$\frac{[H_2S]}{[H_2S]_0} = \left\{ 1 - 2k_1 \frac{1-m}{1-n} \frac{[O_3]_0^n}{[H_2S]_0^{1-m}} \cdot \left[(t/2 + 1)^{1-n} - 1 \right] \right\}^{1/(1-m)} \quad (4)$$

The expression in equation 4 is useful for anticipation and projection whenever the numerical values of the exponents m and n and of the kinetic constant k_1 may be determined.

Experiment

Testing for control of H_2S with O_3 was conducted in a laboratory reactor in a pressure vacuum chamber 80 cm long and 16 cm in diameter, with a temperature of $18 \pm 2^\circ\text{C}$, and atmospheric pressure.

The reactor was supplied with an air flow of 4000 l/hr containing a concentration of H_2S equal to 32-44 ppm and an ozone concentration of 35-130 ppm.

The H_2S air flow was produced by bubbling part of the air in an aqueous solution of Na_2S contained in a one liter flask where a solution of HCl 0.2 N (Fig. 1) was simultaneously dripping.

The ozoned air used in the tests was produced by means of the Ac. Master ozone generator of the Ozono Elettronica Internazionale with the following production capacity:

- 0.6-12 g/h of O_3 with air feed;
- 1.2-24 g/h of O_3 with oxygen feed.

The interior of the reactor was constantly controlled during testing of the elimination of $\text{H}_2\text{O}-\text{H}_2\text{S}-\text{O}_3$.

In particular, progress of the concentration of H_2S was controlled through sampling carried out by means of appropriate specimen removal ports on the sides of the reactor.

Sampling lasted approximately 30-60 sec; the gas was bubbled in an absorption solution of NaOH and ascorbic acid, and the concentration of H_2 was therefore determined by means of potentiometric titration [6].

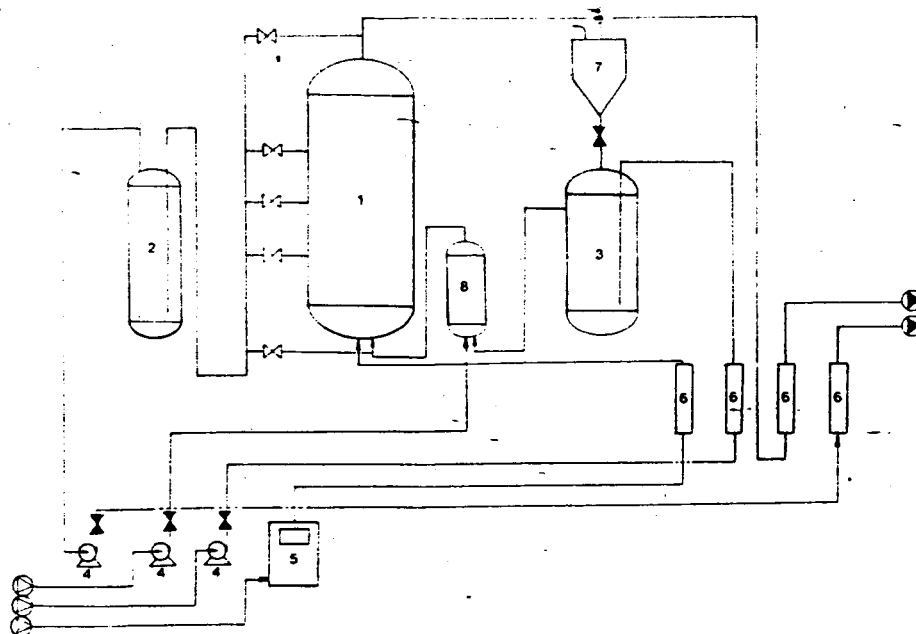


Fig. 1. Diagram of the H_2S production and elimination system through the O_3 oxidation process. (1) Reactor; (2) Sampling system; (3) H_2S production system; (4) Compressors; (5) Ozonizer; (6) Flowmeters; (7) HCl tank; (8) Premixing chamber.

The H_2S concentration profile resulted in a decrease in the first half of the reactor, while remaining almost constant in the second half.

Preliminary experiment results are listed in the table below.

Principal Operating Parameters & Experiment Results /465

G (m^3/h)	$[O_3]_0$ (ppm)	$[H_2S]_0$ (ppm)	t (s)	X (m)	$[H_2S]$ (ppm)	$-\Delta$	$-\Sigma$
4	100	35	3,6	0,20	31	0,98	1,02
			7,2	0,40	30,8	1,03	1,17
4	120	36	3,6	0,20	31,1	1,2	1,23
			7,2	0,40	30,4	1,37	1,40
4	130	32	3,6	0,20	26,6	1,37	1,33
			7,2	0,40	26,1	1,50	1,52
4	35	44	3,6	0,20	42,4	0,362	0,358
			7,2	0,40	42,2	0,407	0,409
			10,8	0,60	42	0,453	0,427
4	130	34	10,8	0,60	27,5	1,63	1,59

Kinetic Equations

From experimental data developed with the conventional least square method, it is possible to determine the values of the kinetic constant k_1 and of exponents m and n of equation 1.

In these determinations, concentrations of ozone and H_2S have been expressed in ppm.

The values obtained are as follows:

$$\begin{aligned} k_1 &= 0,014 [O_3]_0^{-1,5} (s^{-1}) \\ m &= 0,3 \\ n &= 2,5 \end{aligned}$$

With the resulting substitutions, equation 4 becomes:

$$\frac{[H_2S]}{[H_2S]_0} = \left\{ 1 + 0,013 \frac{[O_3]_0}{[H_2S]_0^{0,7}} \cdot \left[(t/2 + 1)^{-1,5} - 1 \right] \right\}^{1/0,7} \quad (5)$$

By means of simple mathematical substitutions, this equation may be written as follows:

$$[H_2S]^{0,7} - [H_2S]_0^{0,7} = 0,013 [O_3]_0 \cdot [(t/2 + 1)^{-1,5} - 1] \quad (6)$$

in which

$$\begin{aligned} \Delta &= [H_2S]^{0,7} - [H_2S]_0^{0,7} \\ Z &= 0,013 [O_3]_0 [(t/2 + 1)^{-1,5} - 1] \end{aligned}$$

The first term (Δ) expresses, even if indirectly, the fractional conversion of H_2S , while the second term (Z) expresses, in parity with the degree of conversion, the staying time as a function of the initial concentration of ozone.

With reference to the experimental values of Δ and Z in the graph (Fig. 2) it is possible to verify the agreement between equation (5) and the same experimental data by means of a single curve.

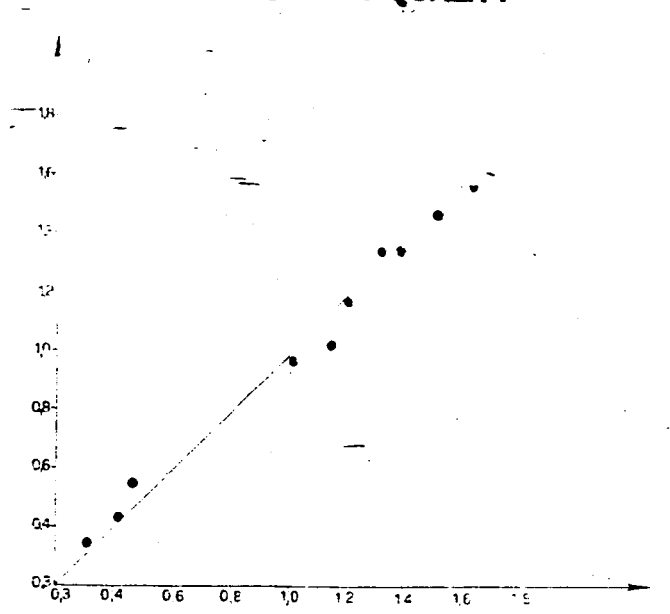


Fig. 2. Comparison Between the Theoretical Model and Experimental Data.

In the measurements taken, the variation interval of Z has been extended from 0.36 up to approximately 1.6. Further increases in this parameter, besides being barely useful in quantifying the kinetic equation, would have little significance in practice.

In fact, from the above we know that Z increases with t and $(O_3)_0$, i.e., with two parameters which do not produce any advantage beyond the limits considered in this study.

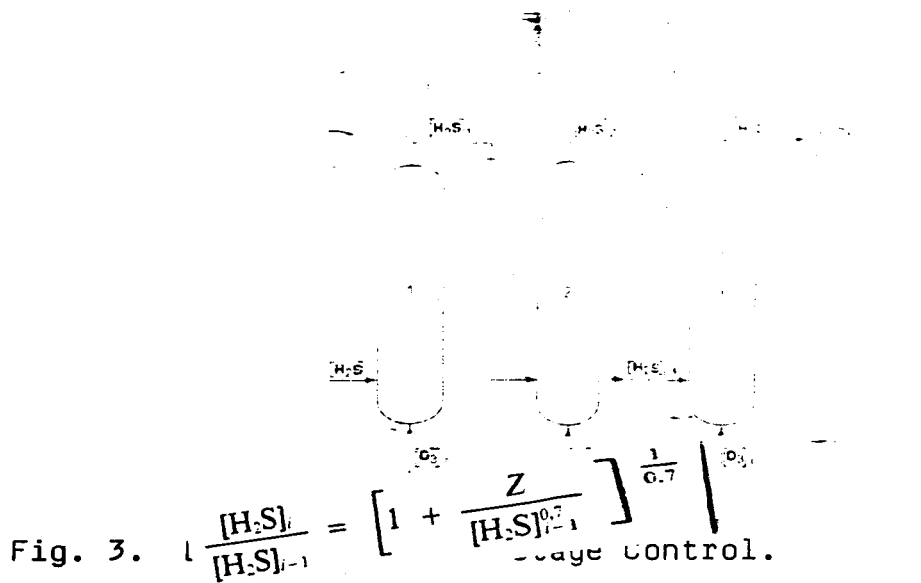
In other words, the increase in Z beyond the value 1.6 would allow corresponding additional increases of time t or of the concentration of ozone (or both). In the first case, the increased holding time would negatively affect the cost of investment without significantly improving the performance of the reactor. In the second case (increase of ozone), which is also costly, quantities of ozone would remain in the final effluent, thereby endangering the external environment.

The use of equation (5) allows a more correct (and, /466 therefore, direct) evaluation of the parameters of the system process and avoids resorting to oversized reactors which would only lead to a useless investment burden.

The results obtained show, in fact, that elimination of H_2S is negligible after times of approximately 4-6 sec, due to the disappearance of the ozone.

In order to achieve greater elimination efficiency, we must resort to higher concentrations of O_3 at the entrance to the reactor, while an increase in volume of ozone which, evidently, implies staying times of 4-6 sec, would be very insignificant.

As an alternative, multi-stage reactors with crossed flows may be used in order to contain the concentration of O_3 at the entrance to the reactor within modest limits (Fig. 3).



The following equation applies to each stage, as can be easily verified through equation (5):

(7)

Conclusions

This study has allowed a quantitative evaluation of the limits (qualitatively noted), imposed on the elimination of H_2S through oxidation with ozone.

In fact, the holding time in the oxidation reactor, which usually supplies a peculiar, somewhat exhausted, resource, is of negligible help in the case examined here.

However, resorting to relatively high concentrations of O_3 in the entrance to the reactor on one hand constitutes a recurring and characteristic solution of the conventional process-system logic, while on the other hand, can be contradicted by problems regarding environmental protection, due to the public health implications currently attributed to the ozone.

Conclusive results for application purposes are certainly premature since they entail measuring the reference performance level. The acceptability of this level (O_3 residue) implies evaluations which are foreign to the scientific-technical competence of the AA.

As previously mentioned, the alternative could be represented by a multi-stage system, as long as the relative investment does not excessively harm the economy of the industrial process requiring control.

A particularly responsive approach to alleviating economic problems is the application of improvement criteria to the reactor system project in cascade.

Presumably, in fact, the usual solution composed of a series of stages of equal volume would not minimize the cost of the operation, since the optimum distribution of the reaction

volumes is strictly tied to the speed of oxidation in each reactor of the cascade.

Additional research is currently underway on this topic, and will be published in a future paper.

Nomenclature

Q_v - volumetric capacity of the treated effluent
 t - time
 X - axial coordinate of the reactor

Footnotes

0 - initial conditions

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